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Horizontal gradient of the chemical speciation of iron in surface waters of the northeast Atlantic Ocean

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Abstract

A transect across the eastern North Atlantic from 42°N, 23°W towards the European continental shelf and English Channel shows a gradient of increasing concentrations of dissolved iron (0.7–1.9 nM), iron-binding ligands and iron(II) across the continental rise. Other data, notably aluminium and manganese, indicate that the increases are part of a front in the metal concentrations, which is due to admixture of bottom waters. Metal fronts in shelf waters are well known, but it was not known that this may include iron(II) and organic iron-complexing ligands. The iron gradient covered a narrow salinity band between 35 and 36, and was linearly related to salinity indicating conservative behaviour, possibly caused by organic complexation keeping the iron in solution. The open ocean iron(II) levels were low but a major proportion of the increased iron levels in the shelf and coastal waters was found to occur as iron(II), and the increase in the overall iron concentration was matched by increased ligand concentrations causing the iron to remain organically complexed. A sedimentary origin for the iron(II) in the surface waters would require iron(II) to be more stable than expected, perhaps through complexation–stabilization.

Keywords: Iron; Organic ligands; Iron(II); Atlantic Ocean

1. Introduction

The vertical gradient of iron in the oceanic water column shows a factor of 10–50 difference between surface and deep water concentrations with a range of 20 pM in the surface waters to 0.7 nM in the deep waters of the North Pacific (Johnson et al., 1997). Horizontal gradients from the continental margin to oceanic regimes are greater as iron levels in coastal waters can be tens of nanomolar (e.g. Nimmo et al., 1989; Schoemann et al., 1998). Continental inputs of iron into the oceans may occur via fluvial (Martin and Meybeck, 1979) and atmospheric pathways (Hodge et al., 1978; Moore et al., 1984; Duce, 1986; Zhuang et al., 1995). Most of this land-derived material is highly refractory and remains in particulate form with little alteration, eventually depositing in deep-sea sediments. The high iron levels in river waters flocculate

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out in estuaries (Sholkovitz, 1978; Sanudo-Wilhelmy et al., 1996) causing the residual iron in the surface ocean to be dominated by atmospheric inputs.

Electrochemical measurements (Gledhill and van den Berg, 1994; Rue and Bruland, 1995) have shown that oceanic iron is fully complexed by organic matter, which enhances the otherwise very low (0.1 nM) iron solubility (Wu et al., 2001). There is also evidence that iron can occur as iron(II) in the upper water column (Waite et al., 1995; Zhuang et al., 1995). Although the stability of iron(II) is thought to be low, and iron(II) is thought to be oxidized in minutes (Emmenegger et al., 1998), there is considerable disagreement between values obtained for its half-life in seawater: at high (μM) levels of Fe(II) its half life is 1.2 min (Millero et al., 1987), whereas a half life of 30–70 min was found at iron levels of 10–40 nM in coastal waters (Zhuang et al., 1995). The former value was obtained in conditions where any natural organic ligands would have been saturated with iron, so this value probably represents the stability of inorganic iron(II); the iron levels in the coastal waters were lower (though still high) and probably to a large extent stabilized by organic complexation. Comparison of the two data sets suggests that organic iron complexation may well greatly stabilize iron(II) when present at low levels.

Previous organic speciation studies have tended to ignore the redox speciation of iron originally present in the samples, and these have not been determined together (de Baar and de Jong, 2001). We present here for the first time measurements of the organic as well as the redox speciation of dissolved iron in surface waters along a transect in the eastern North Atlantic to the English Channel. The concentrations of iron(II) and of iron-complexing ligands were determined by cathodic stripping voltammetry. Due to the nature of the technique, it is likely that not only free (inorganic) iron(II) is detected but also organically complexed iron(II) if present.

2. Sampling and methods

2.1. Sampling

Samples were collected during a cruise (as part of the European MERLIM project), in early spring (March 1998) aboard the Dutch Research Vessel Pelagia (cruise 64 PE 114) in the eastern North Atlantic. Surface samples (~ 2 m depth) were collected travelling north along the 23°W meridian (from 42°N to 45°N) and travelling northeast across the continental shelf into the English Channel to 51°N 2°W, as shown in Fig. 1.

Surface seawater was collected by means of a tube attached to a stainless steel, epoxy-coated, ‘‘fish’’. The fish was deployed about 2 m below the surface, next to the ship and away from the hull. Towing was done while sailing at eight knots. Water was pumped continuously by a peristaltic pump placed in the ship’s laboratory through Teflon tubing; subsamples were taken through a Sartorius Sartobran filter cartridge (0.2 μm with 0.45 μm prefilter) at a rate of 1 l min^{-1}, into clean HDPE sample bottles (500 ml). To check the reliability of dissolved iron data collected by the fish, five comparative samples were taken over a period of 1 h simultaneously from a Zodiac and the fish. This comparison gave good agreement for iron concentrations (de Jong et al., 2000). The samples were stored frozen (− 20 °C) until later determination of the organic iron complexation and the iron concentration by CSV in the Liverpool laboratory. The redox speciation of iron was determined by CSV immediately aboard ship, and also in some frozen samples in the Liverpool laboratory.

The hose was covered with tape, where it was attached to the cable and most exposed on deck and consisted of thick PVC, which is not transparent to UV. There was no UV source in the laboratory (the room had small windows and was without direct exposure to sunlight), and the water went straight from the hose through a thick polyethylene filter cartridge into a polystyrene tube (Sterilin, not transparent to UV) preloaded with bipyridyl to fix the iron(II) over 30 min. The opportunity for significant artificial iron(II) production was therefore minimal.

2.2. Analytical procedures

2.2.1. Reagents

Milli-Q-water (‘‘MQ’’, resistance 18.2 MΩ) was used for reagent preparation and for rinsing. Hydrochloric acid, ammonia and methanol (Merck, Analar grade) were purified by subboiling distillation using a quartz, cold-finger, distillation unit. The pH of a 1 M solution of HEPPS buffer (*N*-2-hydroxyethylpipera-

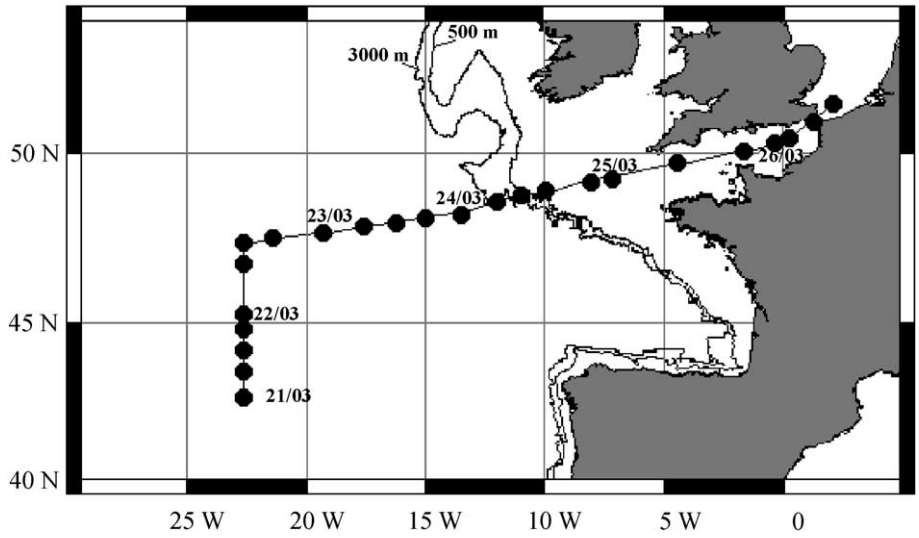

Fig. 1. Map of the sampling locations for the transect in surface waters from the open NE Atlantic Ocean across the continental slope into the English Channel (the main sampling dates are noted).

zine-*N*′-3-propanesulphonic acid, BDH) was adjusted with ammonia to give pH 8 when diluted 100-fold with seawater. Contaminating trace metals were removed by equilibration with 50 μM manganese oxide followed by filtration (0.2 μm). A 0.02 M NN (1-nitroso-2-naphtol) solution in methanol was used without further purification. A stock solution of 0.4 M potassium bromate (Analar) was prepared in MQ and cleaned by equilibration with NN (20 μM) at pH 8 (using HEPPS, 5 mM), followed by extraction using a Sep-Pak C18 cartridge (activated with methanol). A stock solution of 10^{-6} M iron(III) was prepared in 0.01 M hydrochloric acid, from a standard iron solution (BDH Spectrosol); this solution also contained 2.8 mM nitric acid.

Phytoplankton numbers and species composition (of field samples) were determined by flow cytometry (Coulter XL-MCL). The excitation wavelength was 488 nm. Phytoplankton was separated from other particles based on the chlorophyll signal (Long Pass 610 nm). In addition, phycoerythrin (PE) containing species (*Synechococcus*) were assigned using the fluorescent signal of this pigment in the 550–590 nm region (Band Pass 575 ± 20 nm) (Veldhuis et al., 1997).

Aluminium concentrations were determined using a flow-injection application of the lumigallion technique (de Jong et al., 2000). Prior to analysis, sample aliquots of 100 ml filtered acidified seawater (subboiled HNO_3, pH 1.5) in LDPE bottles were buffered by manual addition of clean ammonium acetate buffer to obtain a final pH of 5.5 for inline preconcentration on a column of 8-hydroxyquinoline chelating resin. Typical precision was in the range of 2% at the 15 nM level, the blank was 0.31 ± 0.23 nM and the detection limit (3 sd) 0.69 nM.

2.2.2. Equipment

An Autolab voltammeter (Eco Chemie, The Netherlands) was used for the voltammetric analyses, in conjunction with a Metrohm (Herisau, Switzerland) 663 VA electrode stand (in the hanging mercury drop mode, drop surface area 0.5 mm^2). The reference electrode was double junction Ag/saturated AgCl in 3 M KCl/3 M KCl, and the counter-electrode was glassy carbon. During the adsorption step, solutions were stirred by a PTFE rod rotating at 2500 rpm.

2.2.3. Determination of iron speciation

Iron was determined by catalytic cathodic stripping voltammetry (CSV) using bromate as oxidant (Aldrich and van den Berg, 1998). The "high-labile" dissolved iron concentration was measured after equilibration (1 h) against a high concentration of NN (50 μM NN, added to a voltammetric cell) to obtain close to the total dissolved iron concentration. Comparative measurements were carried out using UV-digested

seawater (90 min, at the original seawater pH), using 10 μM NN. UV digestion (without acidification) has been shown before to efficiently destroy the iron-complexing capacity (Rue and Bruland, 1997; de Jong et al., 2000). The accuracy of the CSV measurements was checked by comparative measurements showing good agreement between FIA-chemiluminescence and CSV (after UV digestion) in samples from the water column (de Jong et al., 2000).

Iron-complexing ligands and the complex stability were determined by titrations with iron with detection of labile iron by CSV using ligand competition against NN (Gledhill and van den Berg, 1994; van den Berg, 1995). Titrations were carried out at pH 8.0 using HEPPS pH buffer and 5 μM NN (Boye et al., 2001). Equilibration was overnight, and the bromate was added 3 min before the first voltammetric scan.

Iron(II) concentrations were calculated by difference between the iron measured before (=labile iron) and after (=labile iron(III)) the addition of a specific iron(II)-binding ligand (10 μM of 2,2-bipyridyl (Bp)) to the filtered sample, using 20 μM of NN, 40 mM of bromate and 0.01 M HEPPS (Aldrich and van den Berg, 1998). The time between the pumping of the seawater from the sea surface next to the vessel and obtaining filtered seawater aliquots was <3 min. Each aliquot was divided over two polystyrene sample tubes (30 ml Sterilins). Bp had been added to one of the Sterilin tubes prior to sampling so the iron(II) was immediately fixed the moment the water passed through the filter and entered the tube. Labile-combined iron was determined by CSV immediately in the aliquot without Bp, and labile iron(III) after 30 min equilibration with Bp.

The detection limit for labile iron was ~0.08 nM, and for iron(II) it was estimated at 0.16 nM as it was based on the difference of two measurements, i.e. the sum of the errors. The detection limit was based on the ability to measure a defined peak, and was not limited by the reagent blank. The actual limit of detection therefore varied somewhat between samples, and at times was less than that quoted.

2.3. Calculation of the organic and inorganic speciation of iron

The ligand concentrations ([L]) and conditional stability constants (K'_{FeL}=[FeL]/([Fe^{3+}][L′])) were calculated by linear least-squares regression of the data fitted to the following equation (van den Berg and Kramer, 1979; Ruzic, 1982; van den Berg, 1982; Boye et al., 2001):

$$[Fe_{labile}]/[FeL] = [Fe_{labile}]/C_L + (\alpha_{Fe'} + \alpha_{FeNN3})/(C_L K'_{FeL}).$$

The inorganic side reaction coefficient for iron (log value) was taken as log $\alpha_{Fe'}=10$ (Hudson et al., 1992), and for $FeNN_3$ a value of log $\alpha_{FeNN3}=12.5$ was calculated using log $\beta'_{FeNN3}=28.39$ (Gledhill and van den Berg, 1994).

The relative standard deviation of repeated (5×) determinations of the ligand concentration was better than 10%, and better than 1% for the conditional stability constant. The standard deviations (STD) for the slope and *y*-axis intercept were calculated using accepted methods for linear least-squares regression for a single ligand fit. The STD for the ligand concentration and stability constant were calculated from the maxima of these STD values.

Concentrations of the free ferric ion [Fe^{3+}], inorganic iron(III) [Fe′], and the organic metal complexes [FeL] were calculated assuming thermodynamic equilibrium, as described before (Boye et al., 2001).

3. Study area

The surface water circulation in the English Channel is generally characterised by a mean flow of Atlantic waters (*S*>35, Lee, 1980) in a northeasterly direction along the shelf, ultimately mixing with alongshore flows of Seine Bay waters (at ~50°N) and English rivers in the Channel and North Sea, illustrated by a salinity decrease, and a nutrients increase, through the English Channel (Fig. 2).

The cruise track covered the continental slope between ~48.6°N 13°W and 49.1°N 8.6°W (Fig. 1). Across the continental slope, the salinity decreased compared to oceanic values, and high gradients of nitrate and aluminium concentrations, *Synechococcus* cell numbers and temperature, were apparent (Fig. 2).

Further northeast, across the continental shelf, the water depth was about 50–200 m, from about 50.36°N 0.31°W through the Dover Strait. The salinity gradient through the Strait of Dover is caused by outflows of

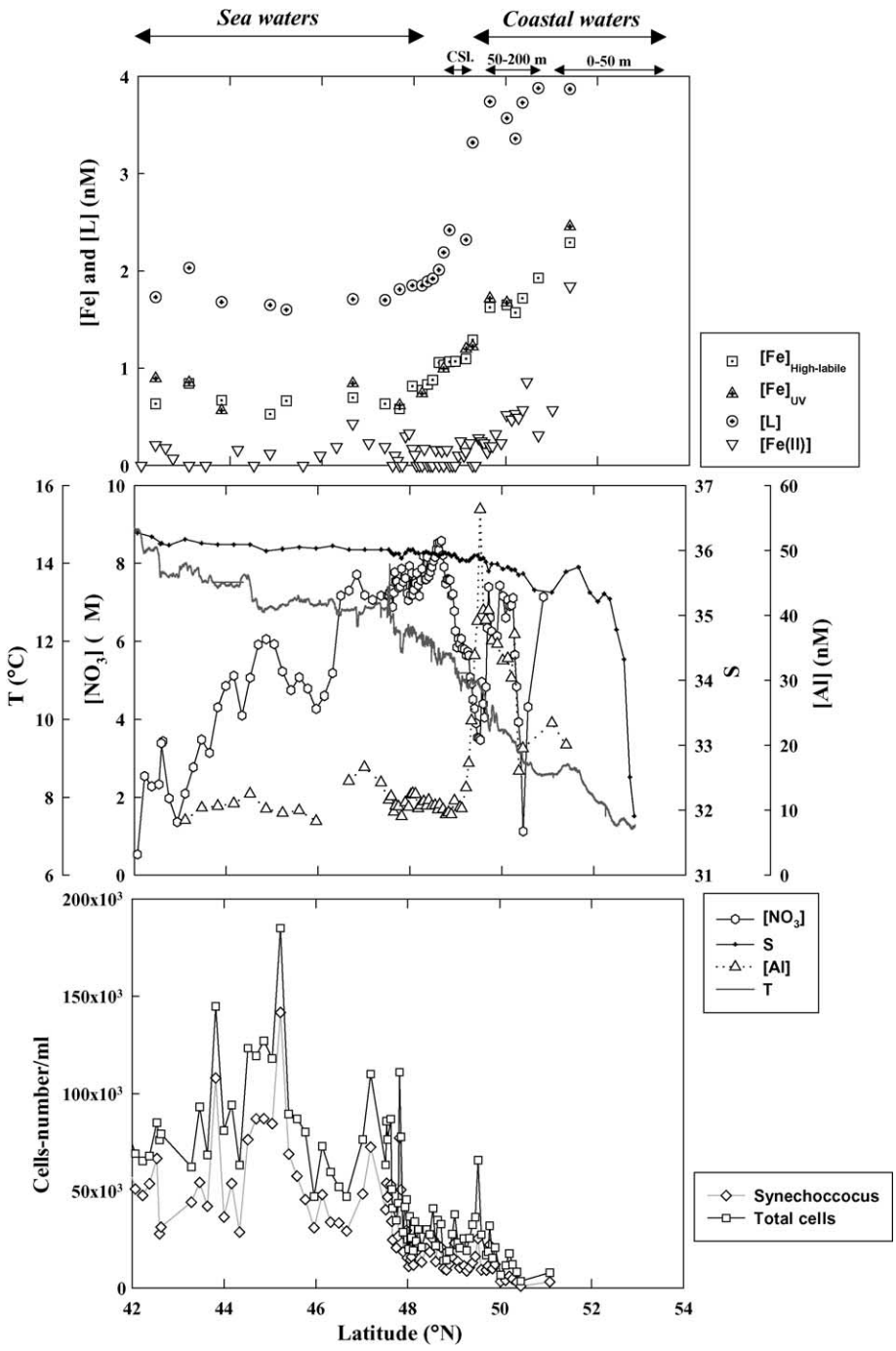

Fig. 2. Surface distribution along the transect (42–54°N) of : (Top) the dissolved iron speciation (dissolved Fe measured as "high-labile" and in UV-digested samples; and [Fe(II)]) and the ligand concentration (L); (Middle) salinity, temperature, nitrate and dissolved aluminium; (Bottom) total phytoplankton (cell-number ml^{-1}), and *Synechoccocus* sp. (cell number ml^{-1}). CSl = continental slope, 50–200 m and 0–50 m indicate the depth of the water column.

the rivers: Thames, Scheldt, Rhine and Meuse. A temperature gradient is also apparent here, due to the shallower depth in this area (Fig. 2).

4. Results

The concentrations of dissolved iron, iron(II) and complexing ligands in the surface waters of the transect are plotted in Fig. 2 along with other parameters. The dissolved iron concentration can be seen to increase steeply when crossing the continental rise (Fig. 2). Low dissolved iron concentrations (<1 nM) in the surface open ocean waters (0.71 ± 0.11 nM, $n=12$) increased to higher concentrations (>1 nM) in the surface waters above the continental slope (1.06 ± 0.02 nM, $n=5$) and higher again above the shelf (1.8 ± 0.27 nM, $n=7$). The dissolved iron concentrations doubled eastward from the continental slope to the Dover Strait, from ~1 to 1.98 ± 0.29 nM Fe ($n=3$) in the shallow waters (50 m) of the Dover Strait. The main increase in the iron concentrations started at the transition between the oceanic waters and the coastal waters (at the continental slope) when the water column depth was still deep (1500 m), so the increase is probably caused by upward transport of iron-rich waters, picking up iron from porewaters along the shelf bottom, and by advection along isopycnals, originating from the shelf some distance away rather than from the sediments immediately below the station. The increases were associated with a decrease in the salinity from 36 to 35.

Along with the iron concentration, the concentration of organic-complexing ligands also increased in the coastal waters, matching the increase in the iron concentration: the iron-complexing ligand concentration was 3.64 ± 0.23 nM ($n=7$) in the coastal surface waters compared to 1.79 ± 0.13 ($n=12$) nM in the oceanic surface waters.

The iron(II) concentrations increased from <0.16 nM (the detection limit) in the oceanic waters to 0.25 nM in the shelf waters and 0.5 nM in the coastal waters (and a value of 1.8 nM at the last station in the North Sea).

The stability of the organic iron complexes varied over an order of magnitude, ranging between 20.5 and 21.4 (log K'_{FeL} values), with an average of 20.8 ± 0.2 ($n=23$). The complex stability in the open ocean (log $K'_{FeL}=20.77\pm0.17$, $n=12$) and coastal (20.85 ± 0.26, $n=7$) surface waters was similar. The average α-coefficient for organic complexation of iron ($\alpha_{FeL}=K'_{FeL}[L]$) was slightly higher in the continental shelf waters ($\sim 10^{12.4\pm0.2}$) compared to waters further away from land ($\sim 10^{12\pm0.2}$) due to the higher ligand concentrations in the shelf waters.

The ratio of organic/inorganic iron ($[FeL]/[Fe']=\alpha_{FeL}/\alpha_{Fe'}$) was 10^2 to $10^{2.4}$, which means that the inorganic iron concentration ($\sim 10^{-11}$ M) was about two orders of magnitude lower than the dissolved iron concentration. In spite of the higher dissolved iron concentration, the average concentration of Fe′ in the surface oceanic waters (12 ± 4 pM $n=12$) was only slightly less than in the surface shelf waters (15 ± 7 pM $n=7$).

5. Discussion

5.1. Dissolved iron

Dissolved iron determinations were carried out by CSV on samples that had been stored frozen. The measurements were without UV digestion to minimise the possibility of sample contamination. A very high detection window was used by adding a high concentration of NN (50 μM instead of 10 μM after UV digestion and 5 μM for speciation) to maximise the fraction of iron complexed by the added NN and minimise a possible nonreactive fraction, which would remain complexed by natural-complexing matter. The stability of the iron complexation by 50 μM NN (log $\alpha_{FeNN}=15.6$) was about 1000× greater than that due to the natural, competitive, complexing ligands (log $\alpha_{FeL}=12.1-12.4$, calculated using the average complex stability and range of ligand concentrations, which are given below), suggesting that a nonreactive fraction should be insignificantly small (less than 1%). This was confirmed by comparative measurements after UV digestion (Table 1 and Fig. 2), which showed that the high-labile iron concentration was equal to the total dissolved iron concentration within the standard deviation of the measurements: ($[Fe]_{UV}=(1.03\pm0.06)[Fe]_{high\text{-}labile}+(0.009\pm0.077)$ nM, $n=12$, $r^2=0.96$), within the concentration range of 0.56–2.5 nM iron. The "high-labile" concentrations were used to calculate the organic speciation of dissolved iron.

The iron concentrations found along the transect (from 0.7 nM in the surface Atlantic to 1.9 nM in the Dover Strait) can be compared to levels between 70 pM (Martin et al., 1993) and 1 nM (Wu and Boyle, 1998) previously found in the surface waters of the NE Atlantic and 17 nM (Statham et al., 1993) for the Dover Strait. Our surface iron concentrations are in good agreement with those (1.0 ± 0.4 nM) found for the same area during a recent survey of the surface Atlantic (Bowie et al., 2002). The consistency of our data contributes to the confidence that we have in its accuracy, which was furthermore checked by comparative measurements of the same samples using chemiluminescence (de Jong et al., 2000). The iron levels are greater than typical for Pacific or Southern Atlantic conditions. However, it is not unusual to find higher iron levels close to the surface (also in the North Pacific, Martin et al., 1989) as the atmosphere is an important source for ocean waters, and the atmospheric inputs in the North Atlantic are relatively large due to the proximity of the Sahara.

The iron concentration was greater than its solubility (0.1–0.2 nM at pH 8.1; Millero, 1998; Wu et al., 2001) in the waters studied here, and it is likely that the iron would have precipitated during the transport of coastal waters to the open ocean, unless the dissolved iron was stabilized by organic complexation. A plot of dissolved iron against salinity between 35 and 36 (Fig. 3) shows a linear dilution line indicating that precipitative iron removal was insignificant over this salinity range. It is likely that the organic complexation (99%) caused the iron to behave conservatively by lowering the inorganic iron concentration to tens of pM (see below), well below the 0.1–0.2 nM solubility limit.

The two boundaries in the iron and ligand concentrations, at 49.28°N 7.5°W and 50.36°N 0.31°W, approximately coincide with boundaries in the concentrations of dissolved aluminium, nitrate (Fig. 2) and manganese (not shown), the latter gradually increasing from 0.5 nM in ocean waters to 2.8 nM in the Strait of Dover (de Jong et al., unpublished results). The changes in the concentrations are associated with the shelf break and with the transition between the coastal waters of the English Channel of 50–200 m deep to the Dover Strait of 0–50 m deep, respectively. In contrast with manganese and iron, the aluminium concentration decreased again in the Channel waters after the boundary. The aluminium concentrations found for the Atlantic and the Channel are in reasonable agreement with those found previously (Measures, 1995; Hydes, 1989). The different behaviour of aluminium is in line with expectation: for instance, in the Pacific, aluminium shows clearly its atmospheric source followed by a decrease by scavenging and an increase due to remobilization (Orians and Bruland, 1986); iron on the other hand follows a clear nutrient-like behaviour (Martin et al., 1989). Similar processes are apparent when the transect crosses the metal front where both aluminium and iron increase but only aluminium shows a steep drop at either side of the boundary (Fig. 2): apparently, the aluminium is subject to rapid scavenging, whereas iron has a more conservative behaviour due to its organic complexation while in the upper water column it is taken up by microorganisms.

The eastward (ocean shelf) increase in the iron concentration is associated with a frontal system on the shelf edge zone (shelf break), which also includes a broad maximum in the nitrate concentration and increased algal cell numbers (Fig. 2). Metal fronts, consisting of relatively steep increases in metal concentrations, are a known feature in shelf waters (Kremling, 1983; Muller et al., 1994; Le Gall et al., 1999) and are due to mixing and upwelling of water masses above the shelf, and this may include the taking of bottom waters, enriched in metals released from the sediments, to the surface. Apparently, this causes the observed increase in the iron concentration. It is interesting that it is associated here with a parallel increase in the complexing ligand concentration. Changes in nutrient concentrations, phytoplankton biomass and primary production are also known to occur in frontal regions (Church et al., 1984; Marra et al., 1990).

East of the frontal boundary, the nitrate concentration and algal cell numbers decreased rapidly, whereas the concentration of dissolved iron continued to increase. The increase in iron was associated with a sharp increase in dissolved aluminium (Fig. 2) indicative of both dissolution of lithogenic material from sediments and of atmospheric inputs of terrigenous material. The highest iron concentrations (1.98 ± 0.29 nM iron, $n = 3$) in the transect were associated with the passage through the Strait of Dover (the lower salinity end member on Fig. 3). Enhanced iron inputs to the surface waters originating from the shelf sediments

Table 1
The dissolved iron speciation in surface waters of the northeastern Atlantic

Date	Time	Longitude (°W)	Latitude (°N)	$Fe_{high\text{-}labile}$ (nM)	$SD_{Fe\text{-}labile}$	Fe_{UV} (nM)	SD Fe_{UV}	[L] (nM)	SD [L]	Log K'	SD log K'	FeL (%)	[Fe′] (pM)	[Fe′] corrctd (pM)	[FeII] (nM)
21 Mar	0:00	−23.01	41.75	–	–	–	–	–	–	–	–	–	–		<LOD
	2:00	−23.01	42.07	–	–	–	–	–	–	–	–	–	–		<LOD
	4:00	−23.00	42.38	0.63	0.11	0.89	0.11	1.73	0.62	20.63	0.03	98.7	13.1	8.8	0.21
	6:00	−23.00	42.60	–	–	–	–	–	–	–	–	–	–		0.18
	10:00	−22.99	42.76	–	–	–	–	–	–	–	–	–	–		0.07
	12:00	−23.01	43.11	0.85	0.12	0.85	0.11	2.03	–	20.78	0.02	98.7	11.6	11.6	<LOD
	14:00	−23.01	43.47	–	–	–	–	–	–	–	–	–	–		<LOD
	16:00	−23.01	43.82	0.67	0.11	0.56	0.07	1.68	0.71	20.6	0.04	97.6	16.0	–	–
	18:00	−22.99	44.17	–	–	–	–	–	–	–	–	–	–		0.16
	20:00	−22.99	44.52	–	–	–	–	–	–	–	–	–	–		<LOD
	22:00	−22.99	44.87	0.53	0.07	–	–	1.65	0.66	20.78	0.02	97.4	7.6	5.9	0.12
22 Mar	0:00	−23.02	45.23	0.66	0.22	–	–	1.6	0.29	21.02	0.11	99	6.7	–	–
	2:00	−23.01	45.59	–	–	–	–	–	–	–	–	–	–		<LOD
Zn	4:00	−23.00	45.96	**0.34**[a]	–	–	–	**1.32**[a]	–	–	–	–	–		0.10
	0:06	−22.99	46.32	–	–	–	–	–	–	–	–	–	–		0.19
	8:00	−23.00	46.67	0.70	0.08	0.84	0.02	1.71	0.56	20.85	0.05	99.6	9.5	3.7	0.43
	10:00	−23.01	47.02	–	–	–	–	–	–	–	–	–	–		0.23
	12:00	−22.99	47.37	0.63	0.07	–	–	1.7	0.46	21.06	0.09	99.3	5.1	3.6	0.19
	14:00	−22.69	47.54	–	–	–	–	–	–	–	–	–	–		<LOD
	16:00	−22.20	47.59	–	–	–	–	–	–	–	–	–	–		0.10
	18:00	−21.70	47.65	–	–	–	–	–	–	–	–	–	–		0.05
	20:00	−21.21	47.69	0.58	0.17	0.62	0.10	1.81	0.54	20.55	0.06	97.8	12.9	12.9	<LOD
	22:00	−20.73	47.75	–	–	–	–	–	–	–	–	–	–		<LOD
23 Mar	00:00	−20.23	47.82	–	–	–	–	–	–	–	–	–	–		0.30
	02:00	−19.74	47.90	–	–	–	–	–	–	–	–	–	–		0.33
	4:00	−19.23	47.97	0.82	0.15	–	–	1.85	0.71	20.58	0.05	99.6	19.8	15.7	0.17
	6:00	−18.73	48.02	–	–	–	–	–	–	–	–	–	–		0.11
Zn	8:00	−18.21	48.06	**0.28**[a]	–	–	–	**1.09**[a]	–	–	–	–	–		<LOD
	10:00	−17.69	48.12	–	–	–	–	–	–	–	–	–	–		<LOD
	12:00	−17.17	48.18	0.77	0.14	0.74	0.01	1.85	0.39	20.82	0.02	98.6	10.6	10.6	<LOD
	14:00	−16.66	48.23	–	–	–	–	–	–	–	–	–	–		0.17
	16:00	−16.15	48.30	0.83	0.03	–	–	1.89	0.36	20.65	0.01	98.0	17.0	17.0	<LOD
	18:00	−15.63	48.36	–	–	–	–	–	–	–	–	–	–		<LOD
	20:00	−15.09	48.41	0.88	0.30	–	–	1.92	0.45	20.88	0.04	98.8	10.9	10.9	<LOD
	22:00	−14.56	48.48	–	–	–	–	–	–	–	–	–	–		0.16
24 Mar	0:00	−14.03	48.55	1.06	0.08	–	–	2.01	0.65	20.66	0.02	97.8	23.2	23.2	<LOD
	2:00	−13.51	48.61	–	–	–	–	–	–	–	–	–	–		0.15
	4:00	−12.99	48.65	1.03	0.07	1.00	0.01	2.19	0.82	20.5	0.08	97.4	26.9	26.9	<LOD
	6:00	−12.47	48.72	–	–	–	–	–	–	–	–	–	–		0.16
	8:00	−11.93	48.78	1.07	0.13	–	–	2.42	0.97	20.65	0.03	98.4	17.1	17.1	<LOD
	10:00	−11.39	48.84	–	–	–	–	–	–	–	–	–	–		<LOD
	12:00	−10.84	48.90	1.07	0.00	–	–	–	–	–	–	–	–		<LOD
	14:00	−10.29	48.97	–	–	–	–	–	–	–	–	–	–		0.10
Zn	16:00	−9.72	49.02	**0.51**[a]	–	–	–	**1.21**[a]	–	–	–	–	–		0.25
	18:00	−9.17	49.09	–	–	–	–	–	–	–	–	–	–		0.10
	20:00	−8.64	49.13	1.10	0.00	1.20	0.09	2.32	0.91	20.99	0.08	99.6	9.0	7.9	0.14
	22:00	−8.10	49.22	–	–	–	–	–	–	–	–	–	–		0.23
25 Mar	0:00	−7.52	49.28	1.29	0.21	1.22	0.12	3.32	0.45	21.4	0.17	99.8	2.5	2.5	0.00
	2:00	−6.93	49.34	–	–	–	–	–	–	–	–	–	–		0.00
	4:00	−6.34	49.41	–	–	–	–	–	–	–	–	–	–		0.28
	6:00	−5.78	49.47	–	–	–	–	–	–	–	–	–	–		0.25

Table 1 (*continued*)

Date	Time	Longitude (°W)	Latitude (°N)	$Fe_{high\text{-}labile}$ (nM)	$SD_{Fe\text{-}labile}$	Fe_{UV} (nM)	SD Fe_{UV}	[L] (nM)	SD [L]	Log K'	SD log K'	FeL (%)	[Fe′] (pM)	[Fe′] corrctd (pM)	[FeII] (nM)
Zn	8:00	−5.25	49.53	**0.59**[a]	–	–	–	**0.40**[a]	–	–	–	–	–		0.23
	10:00	−4.74	49.60	–	–	–	–	–	–	–	–	–	–		0.14
	12:00	−4.19	49.65	1.63	0.06	1.72	0.10	3.74	0.98	20.64	0.03	99.1	17.3	15.2	0.20
	14:00	−3.61	49.71	–	–	–	–	–	–	–	–	–	–		0.20
	16:00	−2.99	49.78	–	–	–	–	–	–	–	–	–	–		0.32
	18:00	−2.34	49.90	–	–	–	–	–	–	–	–	–	–		0.23
	20:00	−1.67	50.02	1.65	0.18	1.67	0.01	3.57	0.62	20.76	0	99.2	14.7	10.1	0.52
	22:00	−1.10	50.13	–	–	–	–	–	–	–	–	–	–		0.47
26 Mar	0:00	0.05	50.21	1.57	0.14	–	–	3.36	0.94	20.68	0.02	99.0	17.9	11.9	0.53
Zn				**1.50**[a]				**1.43**[a]							
	2:00	−0.19	50.28	–	–	–	–	–	–	–	–	–	–		0.49
	4:00	0.32	50.37	1.72	0.16	–	–	3.73	0.93	20.97	0.04	99.8	9.1	6.1	0.57
	6:00	0.89	50.46	–	–	–	–	–	–	–	–	–	–		0.86
	8:00	1.39	50.71	1.93	0.30	–	–	3.88	0.84	20.7	0.01	99.4	19.3	16.2	0.31
	9:37	1.62	51.02	–	–	–	–	–	–	–	–	–	–		0.57
	12:00	2.08	51.40	2.29	0.40	2.46	0.40	3.87	0.44	20.82	0.01	99.4	21.5	4.2	1.84

Dissolved iron ($Fe_{high\text{-}labile}$ and Fe_{UV}), ligand concentrations (L), and the conditional stability constant (K'_{FeL}) are shown along with the standard deviations (SD); the calculated (thermodynamic equilibrium) percentage of iron(III) organically complexed with L (FeL (%)); inorganic iron(III) (Fe′) is shown with (Fe′ corrctd) and without (Fe′) correction for iron(II); and the detected concentration of iron(II). Iron(II) concentrations are indicated as <LOD when there was no significant difference between the measurements with and without Bp. The LOD for iron(II) was estimated at 0.16 nM.

[a] Concentrations of zinc and zinc-binding ligands (Ellwood and van den Berg, 2000) are given for comparison (in bold).

underneath these shallow waters (<50 m), and an associated intensification of vertical mixing by wind stress or by mixing of different water masses from the North Sea and the English Channel with discharges from the Thames, Rhine, Scheldt and Meuse (at the eastern edge of the transect), as well as greater atmospheric inputs due to the proximity of land, may have all contributed to these higher iron concentrations.

The low-oceanic iron concentrations on the oceanic side of the frontal system coincided with the higher number of phytoplankton cells found in the transect (primarily from *Synechococcus*) (Fig. 2). It is thus possible that biological uptake of iron has contributed to removal by scavenging of dissolved iron by biogenic particles to cause the low iron concentrations in these Atlantic surface waters.

5.2. The organic iron-binding ligands

The increase in the iron concentration towards the shelf was mirrored by the iron-binding ligands causing the ligand concentration to remain greater than the iron concentration. The concentration of the ligand was linearly related to that of iron (Fig. 4) with a slope greater than unity: $[L]=(1.67 \pm 0.11)\ [Fe]+(0.16 \pm 0.15)$ nM ($n=23$).

The constancy of the conditional stability constant (Table 1) suggests that there was no systematic change in the detected ligands, i.e. due to a change in ligands from coastal versus oceanic origin.

A plot of the ligand concentration against the salinity revealed a linear covariation (see Fig. 3b) similar to that for iron. As for dissolved iron, the greatest change in the ligand concentration (Fig. 2) occurred in the frontal system of the shelf break. A second, smaller increase in the ligand concentration was associated with the transition from deeper to shallower waters in the eastern part of the English Channel. The parallel increases in the ligand and iron concentrations could suggest that they have the same source, probably from admixed bottom waters, and the actual concentrations are the result of the mixing of the same end members (ocean waters and shelf bottom waters). An alternative explanation could be that the ligand concentration was increased by microorganisms in response to the increased overall iron concentration. Iron-binding ligands in oceanic waters appear to orig-

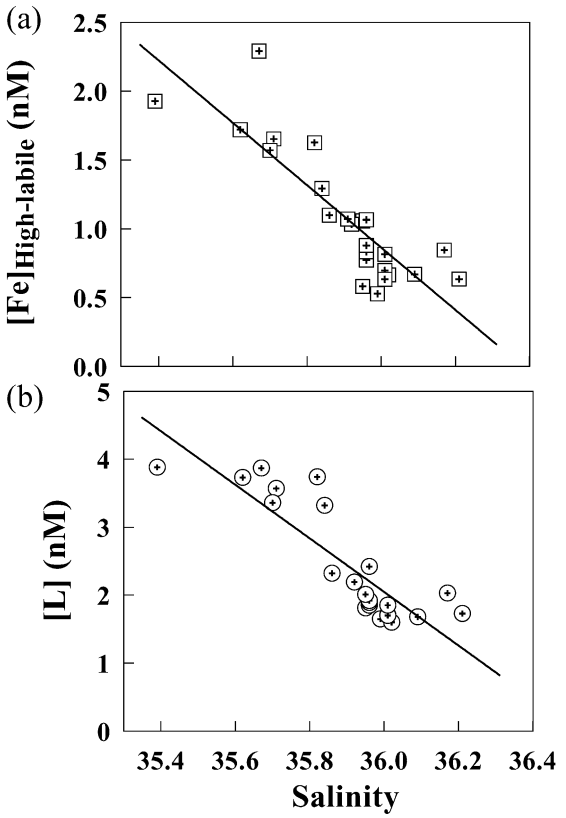

Fig. 3. Dissolved [Fe]–salinity (a) and [L]–salinity (b) diagrams; the linear regressions are given by: $[Fe]_{high\text{-}labile}=(-2.26\pm0.28)S+(82.4\pm10.2)$, $n=24$ and $[L]=(-3.94\pm0.51)S+(144\pm18.2)$, $n=23$).

inate from in situ biological sources (van den Berg, 1995; Rue and Bruland, 1997; Boye et al., 2001). Culture experiments (Boye and van den Berg, 2000) and an oceanic iron fertilization experiment (Rue and Bruland, 1997) have demonstrated that complexing ligands are released by the microorganisms in response to increased iron levels. However, the highest ligand concentrations in the surface waters studied here were not in the waters with the highest cell numbers but with the greatest iron concentrations (Fig. 2), i.e. in those waters receiving the greatest iron inputs. It is therefore not likely that iron at these levels over the shelf would have initiated the release of organic-complexing matter by the natural community, and this was not further investigated.

The concentration of the iron-complexing ligands (2.25 ± 0.7 nM) is 25–50% greater than that of zinc-complexing ligands (average 1.6 nM) in the same waters (Ellwood and van den Berg, 2000) (Table 1). The lower zinc-complexing capacity could suggest specific ligands for iron and zinc, but the difference could also be caused by iron competition: the complex stability with iron is almost $10\times$ greater than with zinc, which could cause the iron to outcompete zinc in case they are bound by the same ligand, and this would also cause the apparent zinc-binding ligand concentration to be less than that for iron (due to masking of L by iron): the average ratio of organic over inorganic iron ([FeL]/[Fe′]) in the transect is 147, whereas the same ratio for zinc is 17, and the iron concentration (~ 1 nM) is twice that of zinc (0.3–0.5 nM), causing iron to outcompete zinc if the same ligand binds both metals.

5.3. Measurement of iron(II) by CSV

The presence of iron(II) at significant levels in these surface waters is perhaps surprising in view of the short half life of iron(II). A half life of 1.2 min was found for iron(II) in seawater (Millero et al., 1987), but this was determined at very high levels (μM) of iron(II), easily saturating any organic-complexing ligands and it should be considered as a half life for inorganic iron. A considerably longer half life of 30–70 min was found at lower but still high levels (tens of

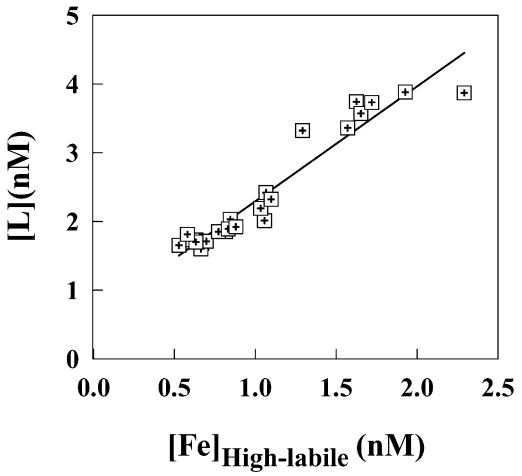

Fig. 4. Relationship between the concentrations of dissolved iron and organic ligands. $[L]=(1.67\pm0.11)\,[Fe]^{+}\,(0.16\pm0.15)$, $n=23$).

nM) of iron(II) in coastal waters, ascribed to organic stabilization (Zhuang et al., 1995). A similar finding to that was made in Australian shelf waters (Waite et al., 1995) at subnanomolar levels of iron(II) albeit in the presence of apparently much higher levels of total dissolved iron (50–400 nM). The possibility that low nanomolar concentrations of iron(II) in oceanic waters may be complexed strongly and thus stabilized for even longer periods has not been eliminated.

The delay between sampling from 2 m depth and the water entering the Sterilin was <3 min, and here the iron(II) was stabilized by the addition of bipyridyl (Bp). The 3-min sampling time was well within the estimated stability period for organically stabilized iron(II) but longer than that for inorganic iron(II). It is therefore likely that the concentration of inorganic iron(II) was underestimated by two half-lives (75%) and that for organically stabilized iron(II) by 5–10%, or less if the organic iron(II) is more stable than estimated previously.

The CSV detection of iron(II) was indirect as it was based on masking iron(II) from the CSV-labile iron fraction by the addition of bipyridyl (Bp). In preliminary recovery experiments, it was established that the Bp binds all freshly added iron(II) (nM levels) within 20 min, whereas additions of iron(III) are not masked (Gledhill and van den Berg, 1995; Aldrich and van den Berg, 1998). The Bp addition did not give false-positives, as it did not react with iron(III) when added at various levels up to 15 nM and over periods of at least an hour, and iron(II) was stabilized by the Bp for periods up to at least 2.5 h. An optimized reaction time of 30 min was selected, which was well within the tested stability periods and shown to be sufficient to bind all added iron(II).

Similar to the ligand competition methods used to determine organic complexation of iron (Gledhill and van den Berg, 1994; Rue and Bruland, 1995), the added Bp would tend to react with organically complexed iron(II) as well as with inorganic iron(II), and this would add to the concentration of iron(II) detected by CSV. Such organically stabilized iron(II) would not be detected for instance by the flow-injection chemiluminescence technique, which is based on the almost instantaneous detection of free, inorganic, iron(II) during its reaction with luminol, and which has been used for recent stability studies (Emmenegger et al., 1998; Powell et al., 1995).

5.4. Distribution of iron(II)

Fig. 2 and Table 1 show low iron(II) concentrations in much of the surface waters, with levels around the 0.16 nM detection limit; however, the levels increased systematically in the shelf and coastal waters, in parallel with the increases in the dissolved iron and ligand concentrations, reaching 1.8 nM iron(II), 80% of dissolved iron in the Channel. The large fraction of iron(II) accounts for most of the increase in the dissolved iron across the shelf and coastal waters.

The low level of iron(II) in most of the oceanic surface waters is perhaps unexpected as iron(II) is thought to be produced from dissolved as well as colloidal iron (Wells et al., 1991). The water here originated from a depth of 2 m where much of the UV would have been lost, and secondly it is possible that the fresh, photolytically produced iron(II) occurred as inorganic iron(II), which would have become largely lost in the 3 min before its fixation aboard ship. The higher iron(II) levels, which were occasionally found in the oceanic waters, suggest that here the iron(II) was stabilized.

The systematic and large increase in the concentration of iron(II) in the shelf and coastal waters was paralleled by a large increase in combined iron, suggesting that the increase is from admixture of bottom waters containing resuspended porewaters, which could be responsible for the increases in the ligand as well as the iron concentrations; for instance, copper-binding ligands are known to be released from sediments (Skrabal and Donat, 1997). This mechanism is supported by the concomitant increase in aluminium.

Alternative sources for the high iron(II) in the shelf and coastal waters could be photochemical reduction of iron(III) (Miller et al., 1995; Voelker and Sedlak, 1995; Kuma et al., 1992), iron(II) from atmospheric deposition (Spokes et al., 1996) and biological reduction of iron(III) (Barbeau et al., 1996). The high iron(II) concentrations occurred in waters with lower algal cell numbers (Fig. 2), suggesting that biological reduction was probably not significant, and there is also no reason why the photochemical effect would have become much stronger in the shelf/coastal than in the oceanic waters. There was also no precipitation event that could justify this as a source. The covariation of iron(II) with combined iron, complexing

ligands and aluminium suggests that the bottom waters constituted the main cause.

The available evidence is that iron in thermodynamic equilibrium is organically complexed (e.g. Gledhill and van den Berg, 1994; Rue and Bruland, 1995; and this work) and it has always been assumed that this is as iron(III). Our data indicate that in spite (or because) of the organic complexation of iron(III), there can be high concentrations of iron(II).

The organic complexation of iron(III) was calculated without taking into account that part of the iron occurred as iron(II) as this was the speciation detected by CSV. The presence of iron(II) was significant only for the samples from the continental rise landwards (those containing higher iron levels). Tests (not shown) using frozen seawater (nine aliquots) showed that the iron(II) was stable and was fully recovered when stored frozen, indicating that it would have been present at the beginning of the titrations. Iron(II) is detected by CSV using NN as if it is iron(III) (without a change in response); this means that if the same amount of iron was still occurring as iron(II) during the titration, then this would have caused high-labile iron concentrations at the beginning of the titrations. This was not the case, indicating that the iron(II) had become oxidized during the equilibration of the samples overnight with the added competing ligand NN. The calculated ligand concentrations and complex stabilities were therefore not affected by the iron(II) originally present in the water.

The estimated percentage (98–99%) of iron(III) occurring as organic complexes (FeL) is not significantly affected by part of the iron occurring as iron(II), but the absolute concentration of FeL is lowered. The concentrations of Fe′ (inorganic iron(III)) are shown in Table 1, with and without correction for the presence of iron(II). It can be seen that the concentrations of Fe′ are lowered by correcting for iron(II) especially in the shelf and coastal waters: a decrease of ~ 20% in oceanic surface waters to 80% in the Dover Strait waters. The effect of this change on what is available to microorganisms is not immediately apparent as both Fe′ and iron(II) could be ‘‘bioavailable’’.

5.5. Iron speciation and iron bioavailability

It has not yet been established which forms of iron (organically complexed iron(III), inorganic iron(III), or iron(II)), are more bioavailable. Recent work indicates that the bioavailable iron may well be inorganic iron(III) (Maldonado and Price, 2000) taken up in a reductive process. The formation of such iron(III) can be enhanced by siderophores (Kuma et al., 2000), followed by the photochemical reduction of iron to transient iron(II), with a subsequent reoxidation to fresh iron(III).

In spite of the greater iron concentration in the shelf and coastal waters than in the oceanic waters, the free iron concentration was almost the same due to the increase in the ligand concentration: calculation based on thermodynamic equilibrium (i.e. without taking the redox speciation into account) showed that the average concentration of inorganic iron was 14 pM in the oceanic waters, versus 15 pM in the coastal/shelf waters. The iron(III) was >99% organically bound in all waters in equilibrium concentrations. In spite of the increase in the iron concentration across the shelf, the inorganic iron concentration showed therefore no systematic trend ($\sim 13.9 \pm 6$ pM along the transect, $n = 23$) due to the increased organic complexation.

Coastal diatoms (*T. pseudonana* and *T. weissflogii*) require 40 and 120 pM of inorganic iron, respectively, to achieve a growth rate of 0.7 day^{-1}, while oceanic isolates are able to grow at this rate at only 3 pM Fe′ (Sunda and Huntsman, 1995). Similarly, the marine cyanobacterium *Synechococcus* sp. PCC7002 has been shown to grow more slowly at 10 pM Fe′ than at higher levels (Trick and Wilhelm, 1995). The inorganic iron(III) concentration in the coastal waters of this study is sufficiently low to limit or reduce growth if these ranges are valid for the algae in these waters. However, it is possible that the algae obtain part of their iron requirement from the organically complexed fraction if this is made bioavailable through photochemical reduction (Maldonado and Price, 2000); in this case, there would be no cause for iron limitation.

The presence of iron(II) shows that these waters are not at thermodynamic equilibrium. The iron(II) presence became especially important at higher iron concentrations across the continental shelf: up to 80% of the dissolved iron occurred as iron(II) (highest in the shelf waters but mostly undetectable in the open ocean waters). In view of bottom waters being a likely source for the high iron(II) levels, the data suggest that the iron(II) in these shelf waters is stabilized by organic complexation.

Iron(II) varied between 0.14 and 0.86 nM (without the highest value of 1.8 nM) in the shelf waters (Table 1), averaging 0.47 ± 0.40 nM ($n = 17$). These values are in the upper range of the cellular requirement of inorganic iron for coastal diatoms to achieve a growth rate of 0.7 day^{-1} (Sunda and Huntsman, 1995), and are also greater than that of growth inhibition of *Synechoccocus* PCC7002 (Trick and Wilhelm, 1995), suggesting that the growth of diatoms and coastal cyanobacteria in these waters is probably not iron-controlled unless the iron(II) occurred in a nonbioavailable form, maybe organically bound. The lower cell densities in the coastal waters, compared to that of the oceanic waters, are more likely due to the cold temperature of the shelf surface waters ($\sim 7-12$ °C), which can be a limiting factor for biomass development (Detmer and Bathmann, 1997), or due to stronger mixing regimes.

Clearly, the iron chemistry is subject to dynamic variations, involving changes in the oxidation state and the transient formation of free (inorganic) iron(II) and iron(III) species at concentrations different from the Fe′ concentrations valid in the equilibrium condition. Any of the transient species could be much more bioavailable, and briefly present at greater concentration than species, which may be thermodynamically more stable. Further work is required to elucidate the importance of the transient species to the marine ecosystem before we can understand how changes in relatively high total iron concentrations can still cause responses (such as ligand releases) in marine microorganisms.

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